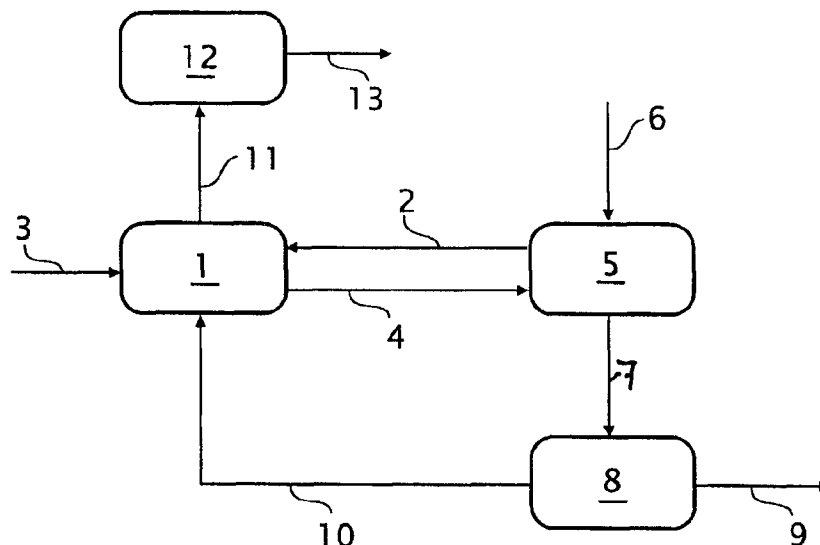




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(21) International Application Number: PCT/EP99/10189 (22) International Filing Date: 17 December 1999 (17.12.99) (30) Priority Data: 98204307.7          18 December 1998 (18.12.98)    EP 60/130,710        22 April 1999 (22.04.99)        US (71) Applicant (for all designated States except US): HOOGOVENS CORPORATE SERVICES BV [NL/NL]; P.O. Box 10000, NL-1970 CA IJmuiden (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): SPORTEL, Heiko [NL/NL]; Het Mollenveld 5, NL-1911 CE Uitgeest (NL). VERSTRATEN, Cornelis, Wilhelmus, Franciscus [NL/NL]; Laurierstraat 74 III, NL-1016 PN Amsterdam (NL). (74) Agent: HANSEN, Willem, Joseph, Maria; Hoogovens Corporate Services BV, P.O. Box 10000, NL-1970 CA IJmuiden (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: METHOD AND APPARATUS FOR THE PRODUCTION OF ALUMINIUM FROM ALUMINA ORE BY ALUMINIUM-SULFIDE PROCESS



## (57) Abstract

Method for the production of primary aluminium from alumina comprising the step of converting alumina into aluminiumsulfide ( $\text{Al}_2\text{S}_3$ ) and subsequently the separation of aluminium from aluminiumsulfide wherein the conversion of alumina into aluminiumsulfide is performed by reacting alumina with  $\text{CS}_2$  containing gas at a temperature  $T_{\text{al}}$  whereby the alumina is mainly  $\gamma$ -alumina. Apparatus for performing the method comprises a first reactor (1) for the manufacture of  $\text{CS}_2$ , a second reactor (5) for the manufacture of  $\text{Al}_2\text{S}_3$  from  $\text{CS}_2$  and  $\text{Al}_2\text{O}_3$ , and a third reactor (8), preferably an electrolysis cell, for the manufacture of Al from  $\text{Al}_2\text{S}_3$ .

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## METHOD AND APPARATUS FOR THE PRODUCTION OF ALUMINIUM FROM ALUMINA ORE BY ALUMINIUM-SULFIDE PROCESS

The invention relates to a method for the production of primary aluminium from alumina ore and to an apparatus for performing the method.

5       The most commonly used method for the production of liquid aluminium from alumina ore is the Hall-Heroult process in which, through electrolysis alumina is decomposed. In this process alumina is continuously fed and dissolved in a bath comprising liquid aluminium and molten cryolite, a mineral comprising fluorides of sodium, aluminium and calcium. A carbon anode is supplied in the bath of molten  
10 cryolite and aluminium. The cell containing the bath, is internally coated with lining of a conductive layer facing the inside and acting as a cathode. Liquid aluminium is formed at the cathode and collected on the bottom of the cell. From there it is periodically removed.

The Hall-Heroult process has a number of drawbacks. One drawback is the  
15 high, electrical, energy consumption. Another drawback is the emission of fluorides such as  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$ , which are considered notorious green house gases, the emission of CO and of heavy metals. Also, the used lining of the cell, known as spent pot lining, is an environmentally unfriendly residu of the Hall-Heroult process. The Hall-Heroult process requires, for a practical production capacity, a large number of cells  
20 which together occupy a large area.

Already more than one hundred years ago an alternative process using aluminiumsulfide has been investigated. The investigation has been taken up again in the 1980s, however without success and the process was not pursued further at that time.

25       US 4,265,716 discloses an embodiment of the aluminiumsulfide based process. In this document it is proposed to react, at a temperature between 1300K and 1500K alumina, carbon and sulfur-containing gas to form aluminiumsulfide and carbonmonoxyde. The sulfur containing gas may include sulfur in one or more of several forms, including  $\text{S}_2$ ,  $\text{S}_6$  and  $\text{CS}_2$ . Further it is mentioned that when the gas  
30 includes carbon as in  $\text{CS}_2$ , it can replace at least a portion of the carbon otherwise introduced as coke or other solids. US 4,265,716 aims at obtaining molten aluminiumsulfide. The molten aluminiumsulfide is then heated to a temperature of about 1600 K to 1800 K and held there for a sufficient time, about 15 to 60 minutes

to cause decomposition to molten AIS and sulfur gas. The molten AIS is then cooled to a temperature sufficient to cause its disproportionation to aluminium and molten aluminium. This disproportionation is performed in the temperature range of 1200-1370 K.

5        Although the invention of US 4,265,716 was published in 1981, the disclosed process has not been put into practice despite the potential advantages of the aluminiumsulfide process. Obviously, in the field of the production of aluminium from alumina, it had turned out that the proposed process was not feasible. Indeed, tests performed by the present inventors have confirmed this. Surprisingly it was  
10       found that the aluminiumsulfide process wherein use is made of  $\text{Al}_2\text{S}_3$  can be performed in a new and inventive manner that is practicable and with which all the advantages as pursued in US 4,265,716 are obtained. Besides, additional advantages over US 4,265,716 are obtained.

      These advantages are obtained with a method wherein the conversion of  
15       alumina into aluminiumsulfide is performed by reacting alumina with  $\text{CS}_2$  containing gas at a temperature  $T_{\text{al}}$  whereby the alumina is mainly  $\gamma$ -alumina like the current alumina used for the Hall Heroult process.

      It was found that, different from what was proposed in the prior art the reaction rate of  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{CS}_2$  is very high compared to the reaction rate between  $\alpha\text{-Al}_2\text{O}_3$   
20       and  $\text{CS}_2$ . Therefore, the method of our invention has the possibility to yield practical quantities of  $\text{Al}_2\text{S}_3$ , within a practical time frame. The method of the invention is based on the following net reaction:



25

COS can be formed as a by-product.

      Tests have shown that the transformation from  $\gamma\text{-Al}_2\text{O}_3$  to  $\alpha\text{-Al}_2\text{O}_3$  takes place in a rather wide temperature range. Therefore, the reaction temperature at which  $\text{Al}_2\text{O}_3$  is converted into  $\text{Al}_2\text{S}_3$  can be chosen within a wide range depending on other  
30       parameters.

      In practice it is preferred that the temperature  $T_{\text{al}}$  is lower than 1100 °C, preferably lower than 1025 °C more preferably lower than 1000 °C.

At temperatures above 1100 °C all  $\text{Al}_2\text{O}_3$  transforms quickly into  $\alpha\text{-Al}_2\text{O}_3$ . The reaction rate of  $\alpha\text{-Al}_2\text{O}_3$  into  $\text{Al}_2\text{S}_3$  by means of  $\text{CS}_2$  proved to be very slow in our experience. Therefore, it is preferred to perform the method according to the invention at a temperature  $T_{\text{al}}$  lower than 1025°C, more preferably lower than 1000 °C. In particular above about 1000 °C the transformation from  $\gamma\text{-Al}_2\text{O}_3$  to  $\alpha\text{-Al}_2\text{O}_3$  progresses very fast. In practice, this means that a substantial portion of the  $\gamma\text{-Al}_2\text{O}_3$  has transformed to  $\alpha\text{-Al}_2\text{O}_3$  before sufficient  $\text{Al}_2\text{S}_3$  has been formed. By operating at a temperature below 1000 °C, a substantial quantity of  $\text{Al}_2\text{S}_3$  can be formed before an impairing quantity of  $\alpha\text{-Al}_2\text{O}_3$  has developed. The conversion of  $\text{Al}_2\text{O}_3$  to  $\text{Al}_2\text{S}_3$  by means of reaction with  $\text{CS}_2$  is also called sulfidation.

Because the method of the invention is performed at substantial lower temperatures than known in the prior art, a considerable reduction in energy consumption can be achieved. Furthermore in the method of our invention solid  $\text{Al}_2\text{S}_3$  is formed, whereas in the prior art method molten  $\text{Al}_2\text{S}_3$  is formed. Therefore, also our method consumes less energy since the melting heat of the formed  $\text{Al}_2\text{S}_3$  is saved.

Preferably the temperature  $T_{\text{al}}$  is higher than 700 °C, preferably higher than 750 °C. Under 700 °C the reaction rate is too low for industrial application.

It is preferred that the conversion of alumina into aluminiumsulfide is performed at a conversion pressure higher than 1 Bar absolute pressure.

Tests have shown that the reaction according to equation (1) progresses faster when it is performed at a conversion pressure higher than 1 Bar, which equals about 1 atmosphere. The reaction rate can further be increased with a further embodiment of the invention which is characterised in that the conversion pressure is higher than 5 Bar, preferably higher than 15 Bar. It has shown that, within practical limits, the reaction rate increases with increasing conversion pressure. Therefore, the conversion pressure is selected at a practical optimum, taking into account such parameters as availability and costs of construction materials for reaction vessels, yield per unit of time and costs and efforts of safety measures.

As mentioned before in the method of our invention, solid  $\text{Al}_2\text{S}_3$  is formed. In practice, it may show that the shape of the particles of the bulk  $\text{Al}_2\text{S}_3$  is not very suitable for further processing. Therefore, another embodiment of the method of the

invention is characterised in that the aluminiumsulfide is at least partly heated to a temperature over its smelting temperature. Although the advantage of less energy consumption is reduced, this embodiment has the advantage that  $\text{Al}_2\text{S}_3$  is available in a reproducible form, suitable for further processing as will be discussed later.

5 In the event that molten  $\text{Al}_2\text{S}_3$  is not needed or wanted at that stage, a further embodiment of the invention is characterised in that the molten aluminiumsulfide is cooled so as to form small-sized grains, having average grain size smaller than the average grain size of the aluminiumsulfide prior to being heated. This embodiment yields  $\text{Al}_2\text{S}_3$  in a form that is easy to handle. Further, this embodiment does not  
10 reduce the advantage of the energy consumption essentially since solidification heat can easily be regained. In one possible embodiment the  $\text{Al}_2\text{S}_3$  particles formed in the sulfidation are slightly raised in temperature whereby the outer surface of the  $\text{Al}_2\text{S}_3$  particles melt. The surface tension causes small-sized densified  $\text{Al}_2\text{S}_3$  droplets or particles to develop. Subsequently, these densified  $\text{Al}_2\text{S}_3$  droplets or particles are  
15 conveyed to a colder part of the reactor e.g. the zone where the sulfidation is taking place, in which the sulfidation takes place, and solidify there. Such densified  $\text{Al}_2\text{S}_3$  particles are easy to handle for further processing.

In the sulfidation process  $\text{CS}_2$  is used as a reactant. Preferably the  $\text{CS}_2$  is formed from sulfur and a carbonaceous reactant. As carbonaceous reactant, coal,  
20 coke, waste materials from the petrochemical industry or waste plastics can be used.

In a preferred embodiment the carbonaceous reactant comprises, preferably contains mainly, methane or natural gas. Methane, in particular in the form of natural gas is available in large quantities and it has the advantage that the production of  $\text{CS}_2$  can take place with both reactants  $\text{CH}_4$  and  $\text{S}_2$  in the gas phase.

25 Carbondisulfide ( $\text{CS}_2$ ) is preferably produced from natural gas and sulfur gas according to the following reaction

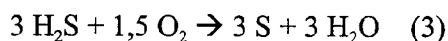


30 This gas phase reaction is carried out in the temperature window 550-650 °C and reaches a conversion of 100%. The reaction is endothermic at these temperature levels and theoretically consumes 1950 kJ per kg  $\text{CS}_2$  when reactants are at 25 °C

and products at 750 °C. Most of the heat input goes into dissociation of sulfur vapor to the reactive species S<sub>2</sub>. In practice 3000 kJ per kg CS<sub>2</sub> are needed.

World-wide production quantity is about 1.100.000 tonnes a year of which 60% is used in the viscose and rayon industry, and 25% for the production of cellophane and carbontetrachloride. Production volume of CS<sub>2</sub> is dropping because cellophane is replaced by other plastic films, carbontetrachloride usage also dropped dramatically because its use as refrigerant and aerosol propellant is driven back. CS<sub>2</sub> mixed with air is an explosive mixture over a wide range of concentrations. Together with the low ignition temperature closed installations working above atmospheric pressure to eliminate leaking in of air (oxygen) are used mostly. All equipment containing CS<sub>2</sub> must be located well away from potential sources of ignition such as open flames, frictional heat, sparks, electrical light bulbs and bare steam pipes. In practice however only installation working with liquid CS<sub>2</sub> have to be protected in such a way. Leakage from hot installation parts will not result in dangerous CS<sub>2</sub> clouds but in small flames where CS<sub>2</sub> reacts with oxygen to CO<sub>2</sub> and SO<sub>2</sub>, thus eliminating danger of explosion.

In the production of CS<sub>2</sub> in accordance with equation (2) also H<sub>2</sub>S is produced. A preferred embodiment of the method of the invention is characterised in that hydrogensulfide (H<sub>2</sub>S) formed in the production of CS<sub>2</sub> is removed and converted to form sulfur which sulfur is returned for the production of CS<sub>2</sub>. The produced H<sub>2</sub>S can be subjected to the following reaction:



The sulfur can be re-used for the production of CS<sub>2</sub>. In this manner the supply of make-up sulfur can be reduced.

Another preferred embodiment is characterized in that unreacted sulfur in the production of CS<sub>2</sub> is removed, preferably by condensation, and returned for the production of CS<sub>2</sub>. In this way, the CS<sub>2</sub> is purified and sulfur is re-used and less sulfur needs to be supplied from external sources.

Yet another embodiment of the method of the invention is characterised in that the CS<sub>2</sub> used is formed essentially from sulfur of which the mainstream results from

the separation of the aluminiumsulfide into aluminium and/or sulfur from the conversion of alumina into aluminiumsulfide. In this embodiment, practically all sulfur used in the conversion of  $\text{Al}_2\text{O}_3$  into Al and by-products, is re-used and only small amounts that inevitably are lost, need to be supplied from external sources.

5       The invention is also embodied in a method in which prior to the conversion of alumina into aluminiumsulfide (sulfidation) the alumina is dried and pressurised, whereupon the sulfidation is performed by passing a gas-solid mixture containing gaseous  $\text{CS}_2$  and solid alumina through a reactor at a temperature of preferably between 800 °C and 900 °C and at a pressure of preferably between 5 and 35 Bar,  
10       whereupon the solids are separated and the gas is further treated for separating unreacted  $\text{CS}_2$  and by-products such as CO, COS and  $\text{S}_2$ , at least one of which is fed back into the process for the production of  $\text{CS}_2$ . In this method the sulfidation is performed in a preferred temperature and pressure range, taking into consideration constructional parameters, energy consumption and unavoidable side reactions. By-  
15       products are to a large extent re-used in the process.

      An embodiment of the invention that is particularly advantageous, is characterised in that the  $\text{CS}_2$  containing gas is formed and essentially fed directly, without essential intermediate storage, to a reactor vessel to react with alumina to form aluminiumsulfide. According to this embodiment it is proposed to integrate the  
20       production of  $\text{Al}_2\text{S}_3$  with the sulfidation and not to acquire  $\text{CS}_2$  from remote production facilities.

      Integrating  $\text{CS}_2$  production with aluminium production in particular with the sulfidation therein has the following advantages:

- No provisions have to be made to store and distribute liquid  $\text{CS}_2$ . Only a  $\text{CS}_2$   
25       storage tank is needed for start-up.
- Further no provisions have to be made to receive and store large quantities of liquid sulfur while the sulfur in this process can be recycled for nearly completely in accordance with other preferred embodiments.
- The final step in the  $\text{CS}_2$  process is normally a distillation to remove  $\text{H}_2\text{S}$  from  
30       the liquid  $\text{CS}_2$  to obtain a 99.9% pure liquid  $\text{CS}_2$ . This step can be optionally omitted while  $\text{H}_2\text{S}$  will have no negative effect on the sulfidation process.



- A totally different reactor design can be applied for the production of  $\text{CS}_2$  from methane or natural gas and sulfur. Generation of hot sulfur gas in the electrolysis of  $\text{Al}_2\text{S}_3$  eliminates the need to vaporize sulfur in the  $\text{CS}_2$  reactor. In the new reactor design the temperature may be chosen higher, making the reaction of methane or natural gas and sulfur exothermic instead of endothermic. This will have the additional advantage in eliminating the use of methane or natural gas as a fuel in the  $\text{CS}_2$ -reactor.
- The off-gas of the sulfidation reactors contains unreacted  $\text{CS}_2$ ,  $\text{S}_2$  and  $\text{CO}$ . This gas can be cleaned in the gas cleaning section of the  $\text{CS}_2$  plant. The  $\text{CO}$  can eventually be fed into the combustion chamber of a Claus unit for the production of sulfur, where it is burned to  $\text{CO}_2$  and will attribute to the production of super heated high pressure steam in the Claus waste heat exchanger.

Preferably the  $\text{CS}_2$  containing gas is essentially  $\text{CS}_2$ . It is not necessary, for the sulfidation, to use essentially  $\text{CS}_2$  as  $\text{CS}_2$  containing gas. However, to avoid possible side reactions and to save energy it is preferred to use essentially  $\text{CS}_2$  as  $\text{CS}_2$ -containing gas.

From the  $\text{Al}_2\text{S}_3$ , produced in the sulfidation, metallic aluminium is to be made. In a preferred embodiment the separation of aluminium from aluminiumsulfide is performed by electrolysis.

As discussed above, the Hall-Heroult process, in which molten metallic aluminium is made through electrolysis, has many drawbacks.

In the 1980's experiments were conducted directed to the production of aluminium in a chloride process in which aluminiumchloride was produced and subsequently subjected to electrolysis. The chloride process was abandoned in 1985. One of the main reasons being the inevitable production of environmentally hazardous chlorinated hydrocarbons during the production of aluminiumchloride. This would lead the skilled person away from applying electrolysis for the separation of  $\text{Al}$  from  $\text{Al}_2\text{S}_3$ .

However the inventors have realised that the electrolysis process as developed for the aluminiumchloride-based process can advantageously be further developed for application in the aluminiumsulfide-based process. The electrolysis of

aluminiumsulfide is a further development of the electrolysis of aluminiumchloride. Similar advantages over the Hall-Heroult process exist, whereas the disadvantages can be less because of the less aggressive nature of sulfur containing gases in comparison to chloride containing gases. Also spent materials like refractory can be  
5 treated more easily to obtain environmentally safe waste products. The spent pot lining from the present process will only contain sulfur and chlorides, but will be essentially free from fluorides and cyanides.

Also the working conditions around the electrolysis cell will be better because the electrolysis cells should be closed to prevent air leaking in and causing oxidation  
10 of the  $\text{Al}_2\text{S}_3$ .

A further embodiment of the method of the invention is characterised in that the electrolysis is performed in a multi-polar electrolysis cell.

The multi-polar cell has the advantage that the voltage drop in the electrolysis process can be reduced due to a low resistance of the cell. Such cell is known e.g.  
15 from US 4,133,727.

Still a further embodiment of the method of the invention is characterised in that the electrolysis is performed directly in a bath of molten aluminiumsulfide.

As an alternative liquid  $\text{Al}_2\text{S}_3$  can be electrolysed directly ( $\text{Al}_2\text{S}_3$  being the most abundant single component in the melt) with only very small amounts and preferably  
20 no external addition of salts to the melt, with or without the use of membranes. The most important advantage of this embodiment is that small inter-electrode space is possible (no lack of feedstock between the electrodes).

The invention is also embodied in an apparatus comprising a first reactor for the manufacture of  $\text{CS}_2$ , a second reactor for the manufacture of  $\text{Al}_2\text{S}_3$  from  $\text{CS}_2$  and  
25  $\text{Al}_2\text{O}_3$  and a third reactor for the manufacture of Al from  $\text{Al}_2\text{S}_3$  said third reactor preferably being an electrolysis cell. Such apparatus has the advantage that the  $\text{CS}_2$  production is integrated with other process steps for the production of aluminium from alumina and that intermediate products need to be conveyed over short distances. This is of particular advantage where intermediate products are aggressive  
30 or at high temperature.

The process of the invention is also referred to as the Compact Aluminium Production Process or CAPP, the key feature of this process, being the conversion of

aluminiumoxide (alumina) to aluminiumsulfide, which can be converted into sulfur (gas) and aluminium preferably through electrolysis.

The invention will now be illustrated in more detail with reference to a non-limiting embodiment according to the drawing in which:

5 Fig. 1 shows a general block-scheme, illustrating the interconnection between the main processes of the method of the invention.

Fig. 2 shows a basic diagram of an apparatus for the production of aluminiumsulfide from alumina and carbonsulfide.

10 In Fig. 1 a simplified block-scheme of the main process steps and their interconnection is shown.

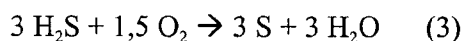
The main two basic unit operations of the process of the invention are:

- the production of aluminiumsulfide ( $\text{Al}_2\text{S}_3$ ) from  $\text{Al}_2\text{O}_3$  using sulfur containing gases;
  - the production of aluminium from  $\text{Al}_2\text{S}_3$  preferably by means of electrolysis.
- 15 Alternatively a disproportionation mechanism may be used as proposed in US 4,265,716.

The main reactions that take place are:



20



Instead of  $\text{CH}_4$ , other carbonaceous materials, such as wood, oil or coal may be used.

25 Another main reaction is the formation of aluminiumsulfide or sulfidation:



30 This process is preferably performed in the range 700 - 1100 °C and 1 - 40 Bar, more preferably in the range 750 - 1000 °C and 5 - 35 Bar. Typically a temperature  $T_{\text{al}}$  of 850 °C and 30 Bar is applied in case solid  $\text{Al}_2\text{S}_3$  is wanted. In the event liquid

or gas  $\text{Al}_2\text{S}_3$  is wanted as feed for the next process step, an appropriate temperature and pressure range can be selected or the formed  $\text{Al}_2\text{S}_3$  can be reheated. Preferably the sulfidation is carried out using essentially only  $\text{CS}_2$  to react with  $\text{Al}_2\text{O}_3$ . Preferably  $\text{Al}_2\text{O}_3$  in powder form or in the form of small-sized particles is used.

5        Preferably, via an electrolysis process aluminium is obtained according to the reaction



Accordingly, the following four main areas of operation can be identified:

- 10        - the production of carbondisulfide gas from natural gas and sulfur;  
          - the production of aluminiumsulfide from aluminiumoxide and carbondisulfide;  
          - the production of aluminium from aluminiumsulfide;  
          - energy recovery.

Returning now to Fig. 1, with reference number 1, the apparatus for the process  
15        for the production of carbondisulfide is indicated.

The preferred process for production of  $\text{CS}_2$  can be shortly described as follows:

High purity liquid sulfur and natural gas or methane are fed via return line 2 and supply line 3 respectively to a reactor vessel (not shown), preferably an externally fired tube reactor. Via return line 2, also CO and  $\text{CS}_2$  are fed back from  
20        apparatus 5 as will be described later. The gaseous reaction product of this reactor vessel contains  $\text{CS}_2$ ,  $\text{H}_2\text{S}$  and  $\text{S}_2$ . This gaseous reaction product is cooled in apparatus 1 to e.g. 150 °C to remove  $\text{S}_2$  by condensation. The liquid sulfur is returned to the reactor vessel for  $\text{CS}_2$ . After the removal of sulfur a mixture of  $\text{CS}_2$  and  $\text{H}_2\text{S}$  remains. These two components are separated in an absorber/stripper section of apparatus 1.  
25        The stream of  $\text{H}_2\text{S}$  gas is purified, i.e.  $\text{CS}_2$  remaining in the stream of  $\text{H}_2\text{S}$  gas is removed, prior to entering a conversion unit, preferably a Claus unit where the  $\text{H}_2\text{S}$  is converted into liquid sulfur which is returned to the reactor vessel for  $\text{CS}_2$  production. In a conventional  $\text{CS}_2$  production facility the stream of  $\text{CS}_2$  gas is purified preferably in a set of distillation towers to obtain high purity  $\text{CS}_2$ . In the  
30        present invention, such high purity  $\text{CS}_2$  is not required and consequently, certain purifying steps can be omitted or simplified. The obtained  $\text{CS}_2$  is fed via supply line 4 to apparatus 5 for the production of  $\text{Al}_2\text{S}_3$  from  $\text{Al}_2\text{O}_3$ .

In apparatus 5, alumina supplied via supply line 6 and  $\text{CS}_2$  supplied via supply line 4 are fed to a  $\text{Al}_2\text{S}_3$  reactor vessel. By-products such as CO,  $\text{S}_2$  and possibly COS and unreacted  $\text{CS}_2$  are returned to apparatus 1 via return line 2.

The produced  $\text{Al}_2\text{S}_3$  from apparatus 5 is fed via feedline 7 to apparatus 8. Apparatus 8 preferably comprises an electrolysis cell for the electrolysis of  $\text{Al}_2\text{S}_3$ . The resulting aluminium is removed via line 9. Sulfur originating from the electrolysis process is returned via return line 10 to the reactor vessel for  $\text{CS}_2$  production in apparatus 1.

Steam, generated in the Claus unit and/or CO resulting from processes in apparatus 1 are fed via feed line 11 to power apparatus 12.

Steam is produced in several locations e.g. the  $\text{CS}_2$ -reactors and the Claus unit. The waste heat exchanger of the Claus unit is the biggest producer and is situated behind the combustion chamber. In this combustion chamber  $\text{H}_2\text{S}$  is (partly) converted to  $\text{SO}_2$  generating a lot of heat. The gas going to the combustion chamber also contains all the CO that was produced in the sulfidation step, this is burned here to  $\text{CO}_2$  also generating steam. Power, in any form, such as steam, or electrical power, is available via power outlet 13.

The production of  $\text{Al}_2\text{S}_3$ , as performed in apparatus 5 of Fig. 1, will now be illustrated with reference to Fig. 2 which shows a non-limitative example of a process flow diagram.

Alumina arrives via supply line 21 (corresponding to supply line 6 in Fig. 1) as a bulk solid preferably in powder form and is stored in silo's 22. From the silo's 22 alumina is transported to a lock-hopper 23 where it is dried and pre-heated, preferably with nitrogen supplied via supply line 54. After drying and pre-heating the alumina is pressurised with small amount of gas, supplied through pressure line 24, preferably gaseous  $\text{CS}_2$ , to the desired pressure, e.g. 31 Bar is chosen before the alumina is charged to a run lock-hopper 25. Components 22, 23 and 25 together form supply means for alumina. With dosing means 26, such as a dosing screw the pressurized alumina is fed via supply line 27 into the main stream of pre-heated pressurized  $\text{CS}_2$ , supplied through pressure line 28 that can be obtained in the following manner.

The CS<sub>2</sub> as produced in apparatus 1 of Fig. 1, is pressurized to 30 Bar with a pump (not shown) before entering through line 30 (corresponding to supply line 4 in Fig. 1) into the CS<sub>2</sub> preheater 31 where CS<sub>2</sub> is vaporized and heated to about 200 °C or higher preferably by condensing high pressure steam supplied through line 32 which was produced in the furnace of the Claus unit as described above. The condensate is removed via line 33. A small side stream of this pressurized, heated CS<sub>2</sub> stream can be used for the injection of alumina through lines 24 and 34.

When the alumina and the CS<sub>2</sub> are mixed the gas/solid mixture is fed via lines 29 and 35 to the sulfidation reactor 36. The gas/solid mixture may be split e.g. into nine separate parts with a so called pepper-box 37 prior to entering the sulfidation reactor or reactors. The sulfidation reactor is preferably an externally fired tube reactor, like the CS<sub>2</sub> reactor vessel of the apparatus in Fig. 1, preferably operated with a operating temperature of about 850 °C and pressure of about 30 Bar. The gas/solid mixture goes through pipes that are heated in a furnace by natural gas burners. Gas and air are supplied via lines 38, 39 and finally 40.

The reaction products (gasses and solids) are separated in a set of two high temperature cyclones 41, supplied thereto through line 53. The gas coming from the cyclones (containing unreacted CS<sub>2</sub>, CO, S<sub>2</sub> and possibly COS) is recycled to the gas treating section of apparatus 1 of Fig. 1 and fed thereto through return line 2. The solid aluminium-sulfide is depressurized in a lock-hopper 42 and sent to a run lock-hopper 43. With a dosing screw 44 the aluminiumsulfide is fed to an intermediate storage silo (not shown) via line 45. As mentioned before it is also possible to choose the operating conditions of the sulfidation reactor 36 such that a liquid Al<sub>2</sub>S<sub>3</sub> is obtained. The liquid Al<sub>2</sub>S<sub>3</sub> may be solidified or may be fed in liquid form into the next process step, such as an electrolysis step.

The off-gas of the sulfidation reactor 36 (i.e. the flue gas of the natural gas burners) can be transported through line 46 to a heat-exchanger 47 and used to heat up gas used for pre-heating and drying, in this case nitrogen. This hot nitrogen is used in a closed loop to dry and pre-heat the alumina in the locker-hopper 23, and fed back to the heat-exchanger through line 48. Make-up nitrogen is supplied through line 49. Fed-back and make-up nitrogen enter heat-exchanger 47 through line 50. A small bleed, removed via line 51, and some make-up nitrogen is needed in

this loop to remove vapour from the recycle stream. The off-gas is removed via line 52.

A series of experiments were performed to test the sulfidation step. In these experiments a sample of  $\gamma$ -alumina (250  $\mu\text{m}$  - 500  $\mu\text{m}$ ) was contacted with a mixture of vaporised  $\text{CS}_2$  and argon gas. Each experiment was characterised by a different temperature or pressure. The following temperatures were tested: 750 °C, 900 °C and above 1000 °C. Also, the pressure was varied from 9 Bars to 20 Bars. The reaction rate was followed by off-gas analysis with a continuous Fourier Transform InfraRed gas analyser. During these experiments the following phenomena were observed: increasing the reaction temperature results in an increased reaction rate, an increased pressure also results in an increased reaction rate and a temperature above 1000 °C results in an less fast conversion than could be expected from extrapolating from the other temperature steps. The main reaction products were sulfur vapour, CO (gas), COS (gas) and aluminiumsulfide (solid). Typical reaction times for a 40 % conversion ranged from 1 hr to 30 minutes with increased temperature and pressure.

The production of aluminium from aluminiumsulfide will be discussed in the following.

It is possible to produce aluminium from  $\text{Al}_2\text{S}_3$  through disproportionation, making use of the fact that  $\text{Al}_2\text{S}_3$  is not stable at high temperatures. The preferred embodiment of the present invention is an electrolysis process. This process step will be illustrated with reference to a non-limitative embodiment of an electrolysis process.

The electrolysis of  $\text{Al}_2\text{S}_3$  is performed in molten fluoride salts or in molten chloride salts in a preferred temperature range of 700 - 1000 °C.

The advantages of electrolysis per se, and in particular over the established Hall-Heroult process are the following:

- Fundamentally the required voltage (0.98 V) for the electrolysis is much lower compared to the classis Hall-Heroult process (1.82 V).
- No chlorine or fluor gas is released from the electrolysis cell.
- The generated sulfur  $\text{S}_2$  does not readily attack carbon (at the temperature and pressure of the electrolysis process no  $\text{CS}_2$  gas is formed).

- The generated sulfur can be used for the production of  $\text{CS}_2$  and thus for the sulfidation of  $\text{Al}_2\text{O}_3$  to  $\text{Al}_2\text{S}_3$  through reaction (1).

This means that also a multi-polar electrolysis cell is possible using (non-consumable) graphite electrodes. Increasing the current density is also very well possible, at the cost of a lower energy efficiency due to the electrical resistance of the melt. Still, the result would be an electrolysis plant with a much smaller footprint.

As in illustration of the electrolysis process, reference is made to an investigation by Minh, who produced aluminium in laboratory scale electrolysis of 5 wt.%  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$  -  $\text{NaCl}$  -  $\text{KCl}$  eutectic (with 10 wt.%  $\text{AlCl}_3$ ) at  $750^\circ\text{C}$  using graphite electrodes (3 cm anode - cathode distance). A current efficiency (CE) of approx. 80 % was obtained at current densities ranging from 0,2 to 1,2  $\text{A}/\text{cm}^2$ .

The voltage drop but not the CE is given for current densities up to 2.0  $\text{A}/\text{cm}^2$ . Interpreting these data, allowing for voltage drops across external connections etc., the power consumption per kg aluminium was calculated (assuming CE = 80 % in all cases). The results are presented in the table below.

current density $\text{A}/\text{cm}^2$	3 cm anode - cathode		2 cm anode - cathode	
	total voltage per cell V	DC Power consumption $\text{kWh}/\text{kg}$	total voltage per cell V	DC Power consumption $\text{kWh}/\text{kg}$
0.8 (Hall Heroult)	2.92	10.9	2.38	8.9
1.2	4.03	15.0	3.32	12.0
2.0	5.79	21.6	4.45	16.5

A current density of 0.8  $\text{A}/\text{cm}^2$  is a common value in the Hall-Heroult process.

Alternatively liquid  $\text{Al}_2\text{S}_3$  can be electrolysed directly (i.e.  $\text{Al}_2\text{S}_3$  being the most abundant single component in the melt), with or without the use of membranes. The most important potential of this alternative is that small inter-electrode space is possible (no lack of feedstock between the electrodes).

In summary, the present invention offers the following advantages.

The operational costs are 30 % lower for the CAPP process when compared to the Hall-Heroult process.



The environmental performance of the CAPP process is excellent while it eliminates the emission of fluorides,  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  (notorious green house gasses), heavy metals and CO completely. Emissions of  $\text{CO}_2$  and  $\text{SO}_2$  are substantially reduced (55 % and 35 % respectively) when compared with the Hall-Heroult process.

5        The use of electric power is 85 % lower for the CAPP process when compared with the Hall-Heroult process.

Next to economical and environmental benefits the CAPP process offers and improvement of the working conditions. Only closed systems are used reducing the exposure of the workers to hazardous components.

10        With the invention it is possible to economically produce aluminium in an environmentally safe way, thereby obtaining the advantages mentioned above.

## CLAIMS

1. Method for the production of primary aluminium from alumina comprising the step of converting alumina into aluminiumsulfide ( $\text{Al}_2\text{S}_3$ ) and subsequently the separation of aluminium from aluminiumsulfide characterised in that, the conversion of alumina into aluminiumsulfide is performed by reacting alumina with  $\text{CS}_2$  containing gas at a temperature  $T_{\text{al}}$  whereby the alumina is mainly  $\gamma$ -alumina.
2. Method according to claim 1, characterised in that, the temperature  $T_{\text{al}}$  is lower than 1100 °C, preferably lower than 1025 °C, more preferably lower than 1000 °C.
3. Method according to claim 1 or claim 2, characterised in that, the temperature  $T_{\text{al}}$  is higher than 700 °C, preferably higher than 750 °C.
4. Method according to any of the preceding claims, characterised in that, the conversion of alumina into aluminiumsulfide is performed at a conversion pressure higher than 1 Bar absolute pressure.
5. Method according to claim 4, characterised in that, the conversion pressure is higher than 5 Bar absolute pressure, preferably higher than 15 Bar absolute pressure.
6. Method according to any of the preceding claims, characterised in that, the aluminiumsulfide is at least partly heated to a temperature over its melting temperature.
7. Method according to claim 6, characterised in that, melted aluminiumsulfide is cooled so as to form small-sized grains, having an average grain size smaller than the average grain size of the aluminiumsulfide prior to being heated.

8. Method according to any of the preceding claims, characterised in that, the CS<sub>2</sub> is formed from sulfur and a carbonaceous reactant.
9. Method according to claim 8, characterised in that, the carbonaceous reactant  
5 comprises, preferably contains mainly, methane or natural gas.
10. Method according to any of the preceding claims, characterised in that, unreacted sulfur in the production of CS<sub>2</sub> is removed, preferably by condensation, and returned for the production of CS<sub>2</sub>.  
10
11. Method according to any of the preceding claims, characterised in that, hydrogensulfide (H<sub>2</sub>S) formed in the production of CS<sub>2</sub> is removed and converted to form sulfur which sulfur is returned for the production of CS<sub>2</sub>.
- 15 12. Method according to any of the preceding claims, characterised in that, the CS<sub>2</sub> used is formed essentially from sulfur of which the mainstream results from the separation of the aluminiumsulfide into aluminium and/or sulfur from the conversion of alumina into aluminiumsulfide.
- 20 13. Method according to any of the preceding claims, characterised in that, prior to the conversion of alumina into aluminiumsulfide (sulfidation) the alumina is dried and pressurised, whereupon the sulfidation is performed by passing a gas-solid mixture containing gaseous CS<sub>2</sub> and solid alumina through a reactor at a temperature of preferably between 800 °C and 900 °C and at a pressure of  
25 preferably between 5 and 35 Bar, whereupon the solids are separated and the gas is further treated for separating unreacted CS<sub>2</sub> and by-products such as CO, COS and S<sub>2</sub>, at least one of which is fed back into the process for the production of CS<sub>2</sub>.
- 30 14. Method according to any of the preceding claims, characterised in that, the CS<sub>2</sub> containing gas is formed and essentially fed directly, without essential

intermediate storage, to a reactor vessel to react with alumina to form aluminiumsulfide.

15. Method according to any of the preceding claims, characterised in that, the CS<sub>2</sub>  
5 containing gas is essentially CS<sub>2</sub>.
16. Method according to any of the preceding claims, characterised in that, the separation of aluminium from aluminiumsulfide is performed by electrolysis.
- 10 17. Method according to claim 16, characterised in that, the electrolysis is performed in a multi-polar electrolysis cell.
18. Method according to claim 16, characterised in that, the electrolysis is performed directly in a bath of molten aluminiumsulfide.
- 15 19. Apparatus for performing the method of any of the preceding claims, comprising a first reactor for the manufacture of CS<sub>2</sub>, a second reactor for the manufacture of Al<sub>2</sub>S<sub>3</sub> from CS<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, and a third reactor for the manufacture of Al from Al<sub>2</sub>S<sub>3</sub>, said third reactor preferably being an electrolysis  
20 cell.

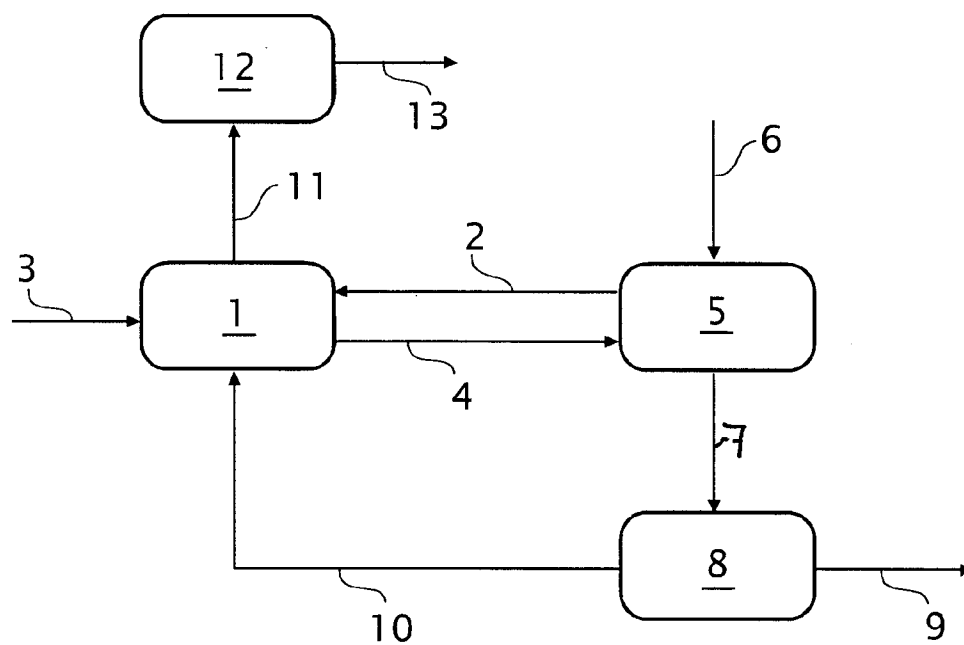


Fig. 1

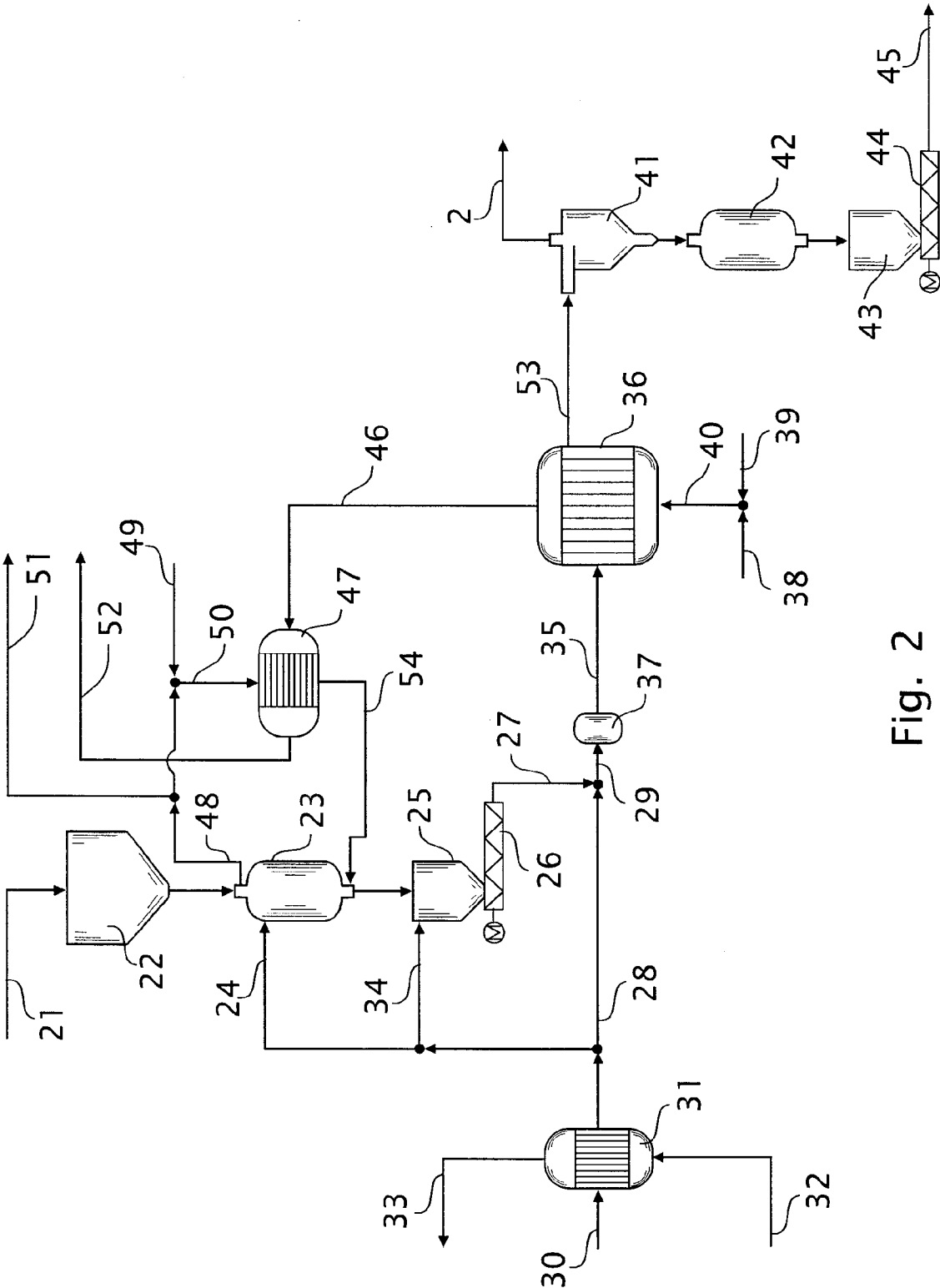


Fig. 2

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/10189

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B21/00 C25C3/06 C01F7/02 C01F7/70

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B C25C C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

18 April 2000

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# INTERNATIONAL SEARCH REPORT

In. ational Application No

PCT/EP 99/10189

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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